Supporting Information

Thiolate/Disulfide Ionic Liquid Electrolyte for Organic Dye-Sensitized Solar Cells Based on Pt-Free Counter Electrodes

HainingTian[a], Erik Gabrielsson [a], Ze Yu[b], Anders Hagfeldt[c,d], Lars Kloo[b,d,*], Licheng Sun[a,d,*]

[a] Organic Chemistry, Center of Molecular Devices, Department of Chemistry, Chemical Science and Engineering, Royal Institute of Technology (KTH), 10044, Stockholm, Sweden. E-mail: lichengs@kth.se

[b]Inorganic Chemistry, Center of Molecular Devices, Department of Chemistry, KTH Chemical Science and Engineering, Royal Institute of Technology (KTH), SE-10044, Stockholm, Sweden. E-mail: larsa@kth.se

[c] Department of Physical and Analytical Chemistry,Center of Molecular Devices, UppsalaUniversity, 75105 Uppsala, Sweden

[d]State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center for Molecular Devices, Dalian University of Technology (DUT), 116012 Dalian, China

1. General

J-V characteristics were recorded using a Keithley source/meter under simulated sunlight from a Newport 300 W solar simulator, giving light with an intensity of 100 mW·cm^{-2}. Incident photon-to-current conversion efficiencies (IPCE) were recorded using monochromatic light from a system consisting of a xenon lamp, a monochromator, and appropriate filters. The different light intensities were calibrated with a different light filter. Both systems were calibrated against a certified reference solar cell (IR-filtered silicon solar cell, Fraunhofer ISE, Freiburg, Germany). The active area of the DSCs studied was 5 mm × 5 mm. A black mask (8 mm × 8 mm) was used in the subsequent photovoltaic studies. Viscosities were determined using a Brookfield CAP 2000+ viscometer. The spin rate used for ionic liquids was 750 rpm and the temperature was set to 25 ^{o}C.

2. DSC Fabrication

FTO glass plates (Pikington TEC 8) were cleaned in the following order: detergent solution, water, and ethanol using an ultrasonic bath. The conducting glass substrates were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 ^{o}C for 30 min and washed with water and ethanol. The screen-printing procedure was repeated 3 times (layer of 2 μm) with TiO_2 paste (Dyesol, 18 NR-T) in order to obtain a transparent nanocrystalline film of a thickness 6 μm and an area of 0.25 cm^2. Two scattering layers (~4μm, Solaronix R/SP) were deposited on the top of the 6μm transparent layer to form the 6+4μm TiO_2 film. The TiO_2 electrodes were gradually heated in an ovenin ambient air atmosphere. The temperature gradient program used included two stationary plateaus at 325 ^{o}C (10 min), and 450^{o}C (30 min). After sintering, the electrodes once again passed, as described above, a (post-)$TiCl_4$ treatment. A second and final sintering, at 450^{o}C for 30 min, was performed. When the temperature was lowered to 30 ^{o}C after the sintering, the electrodes were directly immersed into a 2×10^{-4} MD35EtOH solution for 20 h. The sensitized TiO_2 films were washed with EtOH, dried and sealed with the prepared counter electrode mentioned above using a 25 μm thick hot-melt film (Surlyn, Solaronix) through heating the system at 120 ^{o}C. The electrolyte was filled *via* pre-drilled holes in the counter electrodes using a vacuum procedure, and finally the holes were sealed with a Surlyn sheet and a thin glass cover by heating

3. **Preparation of Counter Electrodes (CEs)**

The CoS CEs were prepared according to the similar method reported in literature.[1] A thoroughly cleaned FTO glass substrate was dipped into a 0.5 M $CoCl_2$ aqueous solution for 30 s, rinsed with ethanol, and dried using a heat gun. The sample was then dipped 30 s into 0.5 M Na_2S aqueous solution, followed by rinsing with ethanol and again a drying step using a heat gun. This process was repeated up to five times in order to obtain the CoS electrode used in this study. PEDOT and platinized FTO CEs were prepared according to our previous methods.[2]

4. Electrochemical Impedance Spectroscopy (EIS)

EIS investigations of DSCs systems were carried out using an Autolab PGstat12 potentiostat with an impedance module operating in the frequency range 10 KHz to 0.1 Hz, using 20 mV AC amplitude, under dark conditions with an applied bias potential (−0.6 V).

Table S1. Photovoltaic results of D35-based DSCs with different CEs and thiolate/disulfide electrolytes.

CE	Light Intensity	J_{sc}	V_{oc}	*ff*	η
CoS[a]	1.0 Sun	3.1	680	0.69	1.5
	0.5 Sun	2.6	660	0.73	2.5
	0.1 Sun	1.04	620	0.68	4.4
	0.05 Sun	0.58	580	0.71	5.0
CoS[b]	1.0 Sun	10.8	670	0.64	4.6
	0.5 Sun	5.6	650	0.69	5.0
	0.1 Sun	0.95	600	0.76	4.4
	0.05 Sun	0.58	510	0.79	4.6
PEDOT[a]	1.0 Sun	3.2	660	0.68	1.4
	0.5 Sun	2.6	650	0.72	2.4
	0.1 Sun	1.03	610	0.68	4.3
	0.05 Sun	0.57	600	0.73	5.0
Pt[a]	0.1 Sun	1.00	630	0.48	3.0

[a] electrolyte **A**; [b] electrolyte **B**

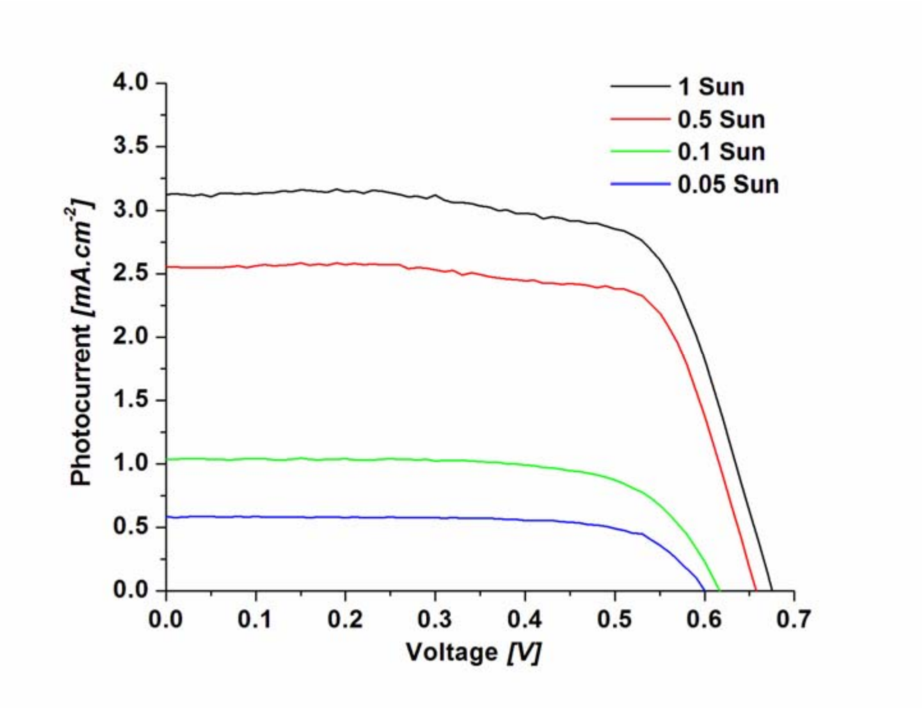

Figure S1. *J-V* curves of DSCs based on the CoS CE and the electrolyte **A** at different light intensities

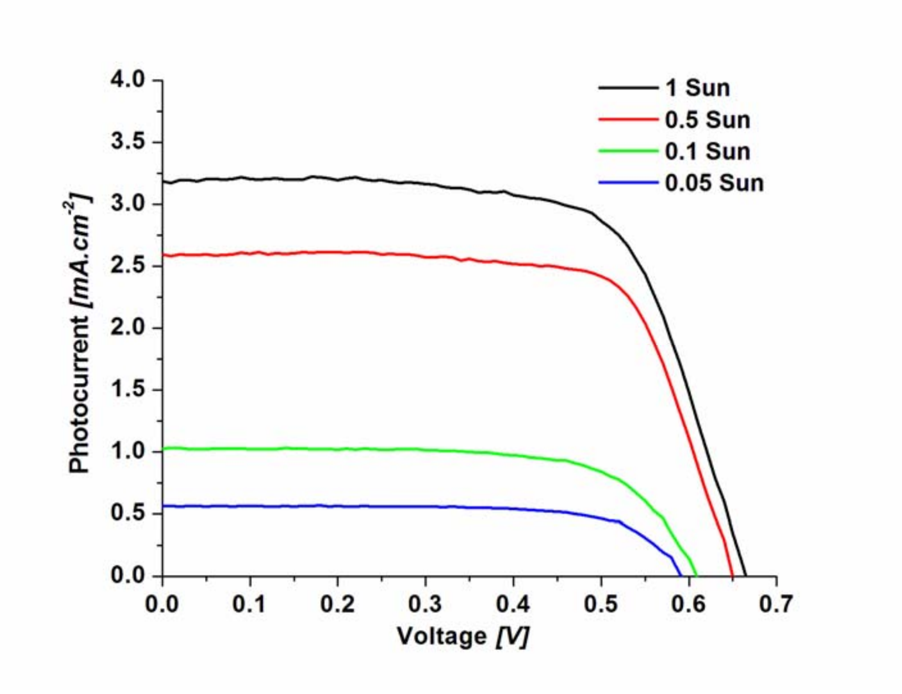

Figure S2. *J-V* curves of DSCs based on the PEDOT CE and the electrolyte A at different light intensities.

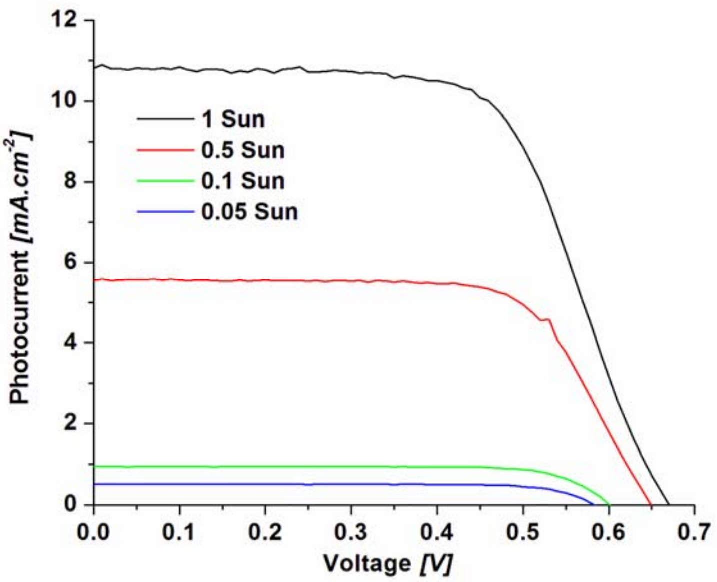

Figure S3. *J*-*V* curves of DSCs based on the CoS CE and the electrolyte **B** at different light intensities.

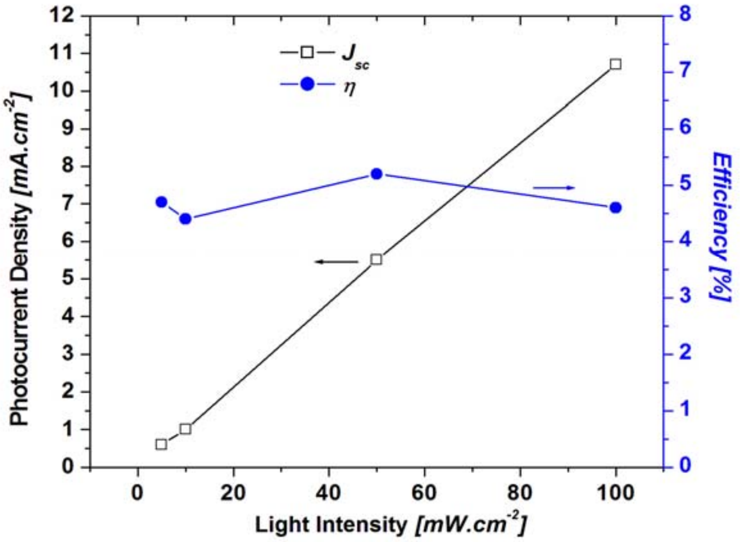

Figure S4. The photocurrent density and efficiency of DSCs based on the electrolyte **B** and the CoS CE at different light intensities.

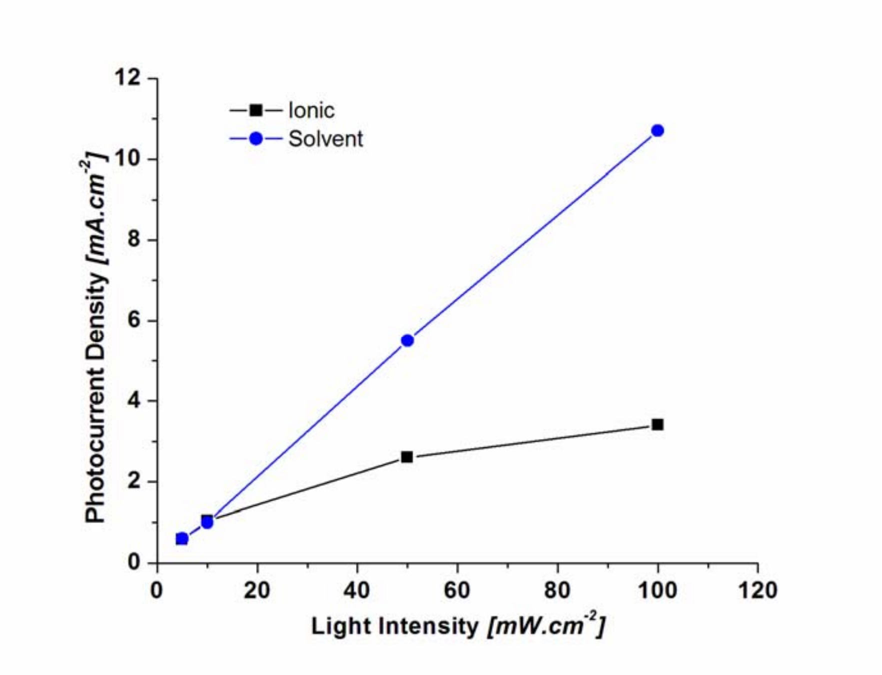

Figure S5.The photocurrent density of DSCs based on the electrolytes **A** and **B** and the CoS CE at different light intensities.

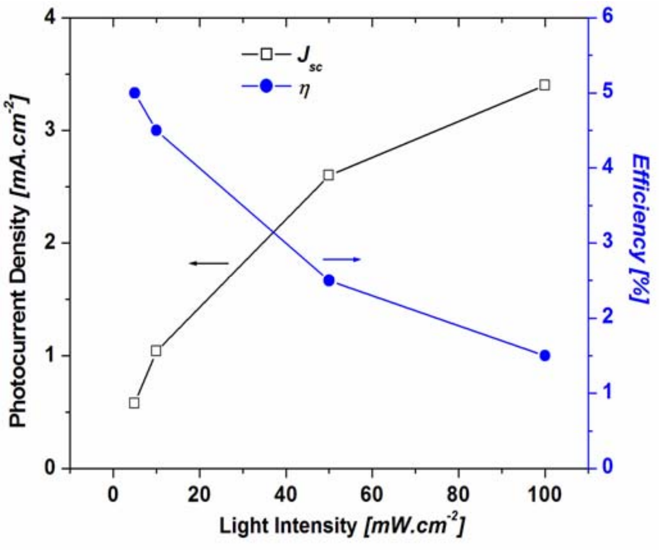

Figure S6. The photocurrent density and efficiency of DSCs based on electrolyte **A** and CoS CEs at different light intensities.

The photocurrent density (J_{sc}) values and efficiencies(η) of DSCs based on electrolyte **A** and CoS CEsat different light intensities. It is clear from the diagram that the J_{sc} values do not depend linearly on the light intensity, which indicates that the electrolyte **A** still displays mass-transport problems. In order to overcome the mass transport issue in this kind of electrolyte, there are many solutions could be utilized to solve the problem in ionic liquid-based electrolyte. First, decrease the viscosity of electrolyte as much as possible. Finding an ionic liquid with low viscosity or a mixture of ionic liquid and organic solvent without diminishing the stability is desirable; Second, reduce the molecular size of thiolate and disulfide compounds. Usually, the compounds bearing with a small molecular size often show fast mass transport ability in organic solvent or ionic liquid. This has been proved in our previous publications;[2,3] Third, increase the concentration of thiolate and disulfide compounds. The solubility of disulfide should be optimized by the structural modification. However, in this case, the recombination reaction between the injected electron and the disulfide compound could be easier to occur, thus yielding a lower photovoltage. The optimization of electrolyte composition should be carefully carried out; Fourth, use a large particle composited semiconductor electrode to overcome the mass transport of ionic liquid in the porous electrode more or less. In this case, a photosensitizer with extremely high molar extinction coefficient is required.

References

1. Z. Yang, C.-Y. Chen, C.-W. Liu and H.-T. Chang, Chem. Commun., 2010, 46, 5485-5487.
2. H. Tian, Z. Yu, A. Hagfeldt, L. Kloo and L. Sun, J. Am. Chem. Soc, 2011, 133, 9413-9422.
3. S. Feldt, E. Gibson, E. Gabrielsson, L. Sun, G. Boschloo and A. Hagfeldt, J. Am. Chem. Soc, 2010, 132, 16714-16724.